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Proceeding

The 2nd International Conference of the Indonesian Chemical Society 2013

ICICS 2013

Research in Chemistry for Better Quality of Environmental

Universitas Islam Indonesia, Yogyakarta, Indonesia
October, 22 - 23th 2013

Abdul Kahar Muzakkir, Conference Hall
Universitas Islam Indonesia (UII), Yogyakarta.
Kampus Terpadu, Jl. Kaliurang KM 14,5 Sleman, Yogyakarta.

Preface

The international conference is an annual conference of the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI). In the year 2013, the mandate of the organizing committee was given to the HKI Yogyakarta branch and also supported by Department of Chemistry of Universitas Negeri Yogyakarta (UNY), Department of Chemistry of Universitas Gadjah Mada (UGM), Department of Chemistry of Universitas Islam Negeri Sunan Kalijaga (UIN Suka), National Nuclear Energy Agency (BATAN Yogyakarta), and Volcano Investigation and Technological Development Center (BPPTK Yogyakarta). For the year 2013, ICICS 2013 is hosted by Department of Chemistry, Faculty of Mathematics and Natural Sciences, Islamic University of Indonesia, Yogyakarta from October 22 – 23, 2013. This conference was also prepared to celebrate 70th anniversary of Universitas Islam Indonesia.

The Sicentific Programme of ICICS2013 comprises the following:

1. Invited Speaker 11 papers
2. A total 256 paper for parallels sessions
   a. Organic Chemistry 32 papers
   b. Inorganic Chemistry 43 papers
   c. Physical Chemistry 37 papers
   d. Analytical Chemistry 68 papers
   e. Education Chemistry 23 papers
   f. Biochemistry 43 papers

The breakdown of the presentation is as follows:

Session	Oral	Poster	Total
Invited Speaker	11	0	11
Organic Chemistry	25	7	32
Inorganic Chemistry	38	5	43
Physical Chemistry	31	6	37
Analytical Chemistry	61	7	68
Education Chemistry	22	1	23
Biochemistry	34	8	43
Total	**222**	**34**	**256**

Yogyakarta, 25th November 2013

ICICS 2013

Editors

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Welcoming Address by The Organizing Committee

Assalamu'alaikum Wr. Wb.

Honorable Rector of Universitas Islam Indonesia
The distinguished invited speakers, and
All participants of the ICICS 2013

Welcome you at the 2nd International Conference of the Indonesia Chemical Society 2013 (ICICS 2013) this morning here at the Auditorium Kahar Muzakkir Universitas Islam Indonesia, Yogyakarta. The international conference is an annual conference of the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI). In the year 2013, the mandate of the organizing committee was given to the HKI Yogyakarta branch and also supported by Department of Chemistry of Universitas Negeri Yogyakarta (UNY), Department of Chemistry of Universitas Gadjah Mada (UGM), Department of Chemistry of Universitas Islam Negeri Sunan Kalijaga (UIN Suka), National Nuclear Energy Agency (BATAN Yogyakarta), and Balai Penyelidikan dan Pengembangan Kegunungapian (BPPTK Yogyakarta). For the year 2013, the honor of hosting ICICS 2013 has been given to the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Yogyakarta. This conference was also prepared to celebrate 70th anniversary of Universitas Islam Indonesia.

The conference comprises both oral and poster presentation in English and Indonesian with optional post conference publication of full papers in English in the Procedia Chemistry (Elsevier, ISSN: 1876-6196) and Proceeding Conference for Indonesian language. There are 211 papers presented orally and 34 papers presented by poster covering wide-variety subjects of chemistry. We invited 6 Indonesian invited speakers, 2 Japan invited speakers, 1 Australian invited speakers, 1 Saudi Arabia invited speakers, and 1 Malaysian Invited speakers.

We hope you will enjoy a pleasant and valuable seminar at Universitas Islam Indonesia

Wassalamu'alaikum Wr. Wb.

Riyanto, Ph.D.

ICICS 2013

Chairman

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Opening Speech from the Rector of Universitas Islam Indonesia

Assalamu'alaikum Wr. Wb
The distinguished invited speakers, and
All participants of the ICICS 2013

Firstly, I would like to express my great appreciation to the Department of Chemistry UII as one of the organizers of the program The 2nd International Conference of the Indonesian Chemical Society 2013 (ICICS 2013) with the theme "Research in Chemistry for Better Quality of Environmental". I am proud that this interesting event is being organized and held in Yogyakarta.

As the biggest and the oldest private university in Yogyakarta, University Islam Indonesia is committed to the excellence in research and teaching. Recently, we are preparing UII as one of the world class universities.

Knowing that committee has selected outstanding speakers from various prestigious institutions. I believe that all of the participants will enjoy the discussion of issue covered by the topic of this seminar. Scientist have shown that the environment's condition is increasingly critical, and human industrial activities are largely to blame. In fact that environmental damage is a crisis we caused together, therefore, a responsibility we all share together. We are deeply concerned with the issues and opportunities in the internationalization of sciences for better life, sciences have to make better quality of environmental.

Finally, I would once again like to thank the organizer for organizing this event, and to thank all the participants attending this ICICS 2013 event as well as delivering their scientific presentations. I do really hope that you can enjoy this seminar and have excellent stay in Yogyakarta.

Wassalamu'alaikum Wr. Wb

Prof. Dr. Edy Suandi Hamid, M.Ec.
Rector of Universitas Islam Indonesia

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Remarks by the Chairman of the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI)

Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI) is an independent, nonprofit organization founded in February 1962 to facilitate communication among Indonesian chemists and other professionals from chemistry related fields, and to promote the advancement of science, education, and application of chemistry to support the better life of mankind. HKI organize activities to enhance communication and collaboration among chemists in various institutions in Indonesia, to disseminate new knowledge and research results in chemistry and related fields, to improve the knowledge and skills of chemists working in schools, universities, industries, research institutes, and other sectors, to nurture a scientific temper on school children to ensure strong capabilities of future chemists that are needed for humankind, and other activities that support its missions. HKI holds various academic conferences, publishes several journals, supports the development of scientific information systems in Indonesian; organize training for chemists in various sectors, etc.

The 2013 International Conference of the Indonesian Chemical Society will be the 2nd event in the ICICS conference series, started in 2012, that brings together individuals involved in chemistry-related fields (chemistry, pharmacy, environmental science, chemical engineering, molecular biology, material science, education chemistry, etc.) or institution in chemistry-related sectors. The First International Conference of the Indonesian Chemical Society 2012 is organized by East Java Branch of HKI in collaboration with chemistry departments at several universities in East Java: ITS, UB, UIN Maliki, UM, UMC, Unair, Unej, and Unesa.

ICICS 2013 will be organized by the Indonesian Chemical Society Yogyakarta branch. The international conference was supported by the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI), Department of Chemistry of Universitas Negeri Yogyakarta (UNY), Department of Chemistry of Universitas Gadjah Mada (UGM) and Department of Chemistry of Universitas Islam Negeri Sunan Kalijaga (UIN Sunan Kalijaga). For the year 2013, the honor of hosting ICICS-2013 has been given to the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia (UII), Yogyakarta, Indonesia.

Congratulations to the ICICS 2013 committee for this conference.

Dr. Muhamad Abdulkadir Martoprawiro
Chairman of the Indonesian Chemical Society

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Reaction Study of Phenol Hydroxylation on Al/Fe Pillared and HDTMA Intercalated Bentonite Catalyst

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Abstract

The phenol hydroxylation reaction over Al/Fe Pillared and HDTMA intercalated bentonite has been studied using batch system. The effects of the preparation methods on the catalytic performance of modified bentonite were investigated. Natural bentonite was modified by direct and indirect pillarisation. In direct method, Al and Fe ions were used as pillaring agent to produce a bigger clay pore size. In indirect method, the first step was intercalation process to insert organic surfactant molecules (HDTMA) inside the clay molecules, and then the next step was pillarisation process using Fe cationic. Pillarisation of natural bentonite and HDTMA-bentonite with Fe metal has been done in various mol Fe solutions. The ratio of bentonite and intercalating agent or pillaring agent was 1 gr/50 ml. The mixture was agitated, and then the solid phase was washed with distilled water until free of chlorine ion. Then it was dried and calcined at 450 ^oC for 6 hours in N_2 and O_2 atmosphere. The modified bentonites were characterized by FT-IR spectrometer.
The catalytic reaction was conducted by entering both catalyst and phenol into batch reactor and then the mixture was heated. The reaction was conducted at 70^oC for 4 hours. Along reaction (after temperature 70^oC reached), solution of H_2O_2 was added stepwise into reactor during reaction. Molar ratio of phenol to H_2O_2 is 1 : 1. The weight ratio of catalyst to phenol was 1:10, and concentration of phenol is 1 M. The observed variables were catalyst activity and selectivity. The catalyst activity was observed as phenol conversion, and the selectivity was observed as selectivity of wanted product (hydroquinone).
The presence of Fe-pillared bentonite catalyst in the phenol hydroxylation reaction will give effect on increasing catalyst activity. It happens because number of active site and suitable pore size increase so that the amount of phenol, which can be converted into product, will also increase. It gives impact on selectivity of hydroquinone, cathecol, and benzoquinone will also increase. Finally, as conclusion the optimum performance of catalyst is PILB HDTMA 0.1 % Fe 1 mmol in the phenol hydroxylation reaction.

Keyword: bentonite, pillarisation, intercalation, phenol hydroxylation, hydroquinone

Introduction

Clay is one of the most abundant material found in nature, especially in Indonesia. Bentonite, one of material kind of clay, which is used in this research, is natural bentonite from Tulakan, Pacitan in east Java. Bentonite is generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$. Up to now, bentonite can be utilized as filler, ion exchanger, catalyst, adsorbent etc.

Bentonite has characteristics such as moisture content as high as 30-40 %, and easy to be swelling. Because of the properties, the potential of bentonite application has recently

attracted a lot of attention in both academia and industry, which concern the understanding of maximize the existing potential. The characteristics cause unstable structure and make low selectivity for both adsorbent and catalyst. Otherwise, the interlayer spacing of the swollen clay is sufficient to receive the Al and Al/Fe polyoxocations [1]. Because of that, bentonite has to be modified to get more stabile structure. One of the ways to modify bentonite is by pillarization process [2]. The application fields of these substrates are very broad because of the possibility to intercalate different types of pillars making them suitable for specific adsorption and catalytic processes.

The introduction of inorganic pillars in the natural bentonite improves its resistance and stability, increases its micro porosity and provides larger surface area and accessibility to its acid sites (Brönsted and Lewis sites) [3],[4]. Pillared bentonite can be utilized as catalyst because of the reason that pillared bentonite has active sites such as silica group (SiO_4) and alumina group (AlO_4). The presence of active metal which is penetrated into bentonite structure during pillarization process can enhance the catalytic performance of pillared bentonite. Other wise, the presence of pore which has definite size will give the ability to select both of reactants and products.

Various works have been reported on the catalyst synthesis. They show that catalytic activity depends on several factors such as chemical composition, preparation method, calcinations temperature and characteristic of catalyst surface.

In environmental catalysis there is a great interest in obtaining pillared clays containing iron (oxides or oxyhydroxides) species use in the catalytic wet peroxide oxidation of toxic organic compounds since many industrial processes yield a variety of organic contaminants which are poured into natural water sources with negative impact on ecosystem and humans (toxicity, carcinogenic and mutant properties) [5]. Among these pollutants contained in industrial residual water we can highlight phenol, substituted phenols (chlorophenol, nitrophenol), oxalic acid, acetic acid, pesticides and herbicides [5]-[8]. Phenol is particularly considered as one of the most toxic organic contaminants and it is commonly chosen as model molecule on catalytic oxidation of organic compounds studies in diluted aqueous medium [9].

This work shows the synthesis of solid catalyst, bentonite pillared with Al/Fe and intercalated with HDTMA, in which iron is introduced as active phase (activation sites for hydrogen peroxide as well as organic molecules) in order to develop the catalyst material to the complete oxidation of organic molecules.

Experimental

Catalyst preparation

The starting clay was a natural Pacitan bentonite, extracted from Pacitan region, East Java. The pillaring agent solution was prepared by mixing NaOH and Fe (and NaOH Al/Fe 1 mmole) which has molar ratio OH to Fe = 0.8 (and OH to Al/Fe = 0.8). he intercalating agent solution was prepared by mixing HDTMA 0.1% solution and bentonite suspension which has total volume of solution was 1 L. Pillarization process of the clay was carried out by mixing bentonite and pillaring agent solution with ratio [gram bentonite/volume of solution] = 1 gram/50 mL. The mixture was heated at 70-75 ^{o}C. After 5 hours, the mixture was cooled, and washed with aquadest. The obtained solid was dried in the oven at 100 ^{o}C. After pillarization process, bentonite was calcined at 500 ^{o}C for 4 hours with nitrogen and oxygen stream.

Characterization of the catalyst

The chemical analysis of the solids was carried out by Fourier Transform Infra Red Spectrophotometer (FTIR, Bruker Tensor 27, Germany) to characterize bentonite structure. The amount of Fe was analyzed using Genesys 6 UV-Vis Spectrophotometer.

Catalytic activity

The catalytic oxidation reaction of phenol in a diluted aqueous medium was carried out in a batch glass reactor equipped with thermometer, and reflux condenser. It is open to the atmosphere, and thoroughly stirring with magnetic stirrer. Firstly, the reactor was loaded with phenol solution and catalyst and heated up until 70^{o}C. The reaction was conducted at 70^{o}C for 4 hours. The hydrogen peroxide solution was added stepwise during a reaction time of 4 hours. The molar ratio of phenol to hydrogen peroxide = 1:1, weight ratio of catalyst to phenol = 1:10. The course of the phenol conversion and selectivity was followed by high performance liquid chromatography (HPLC) by means of Knauer.

Results and Discussion

Characterization

Fig.1. depicts FTIR spectra of the catalyst materials, i.e. fresh bentonite, Fe pillared bentonite with HDTMA 0,1 %, Fe pillared bentonite, Al-Fe pillared bentonite with HDTMA 0,1 % and AL-Fe pillared bentonite.

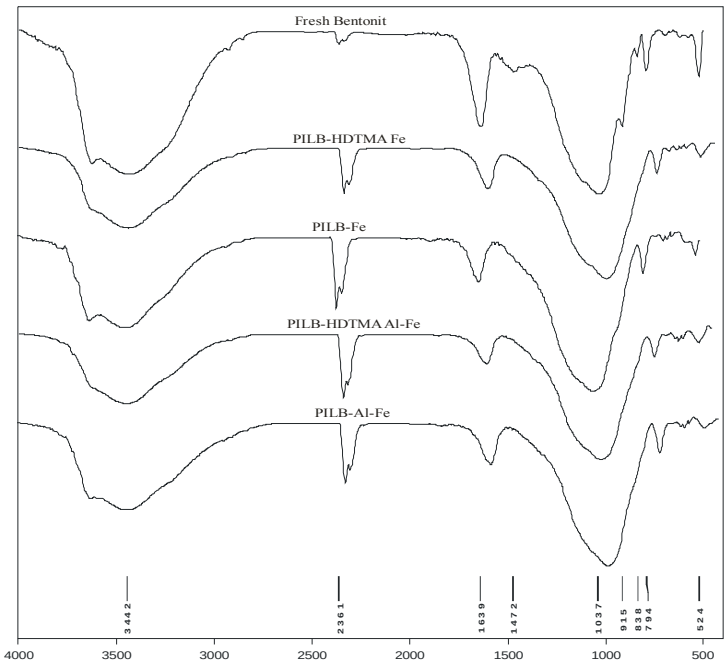

Fig. 1. FTIR Spectra of fresh bentonite, PILB-HDTMA 0,1 % Fe 1 mmole, PILB-Fe 1 mmole,
PILB-HDTMA 0,1 % Al-Fe 1 mmole (1:1), PILB-Al-Fe 1 mmole (1:1), after calcination

The broad absorption peak at 3442 cm^{-1} indicates the presence of stretching asymmetric –OH group. It is supported by the absorption peak in the region 1638 cm^{-1} which is indicated stretching symmetric H-O-H of water. The absorption peak at 3626 cm^{-1} appears clearly for all of material because bentonite has naturally –OH group in the form of Al-OH, and Si-OH in the matrix polymer.

The absorption peaks in the region 1030 – 1040 cm^{-1} indicate asymmetric stretching O-Si-O and O-Al-O group in tetrahedral structure TO_4 (T = Si or Al) of clay structure. The peak would be appeared wider after pillaring process with Fe because of the new formation of polymer system O-Al-O and O-Si-O in pillared bentonite. Figure 1 also shows the broad absorption peak in the range of 950 – 1200 cm^{-1} but not significant. The peak indicates asymmetric stretching of O-Fe-O in pillared bentonite structure. It reflects the presence of metal Fe which penetrates, forms pillars and supports layers in the bentonite structure as Fe oxide. However the spectra show that the number of Fe is not significant. It can be shown from table 1 that the amount of Fe which penetrates in each sample is not too different from it in the absorption peak in the range 950 – 1200 cm^{-1}.

Table 1. The amount of Fe which penetrates in bentonite structure

Sample	The amount of Fe (mg/g bentonite)
PILB Fe 1 mmole	4,8088
PILB Al-Fe 1 mmole (1:1)	3,5147
PILB HDTMA 0,1% Fe 1 mmole	5,0147
PILB HDTMA 0,1% Al-Fe 1 mmole (1:1)	5,1029

The highest amount of Fe which penetrates into bentonite is PILB-HDTMA 0,1 % Al-Fe 1 mmole (1:1) and PILB HDTMA 0,1 % Fe 1 mmole. The result is validated by the IR result at figure 1 where the broadest absorption peak in the range 950 – 1200 cm^{-1} is PILB HDTMA 0,1 % Al-Fe 1 mmole (1:1) and PILB HDTMA 0,1 % Fe 1 mmole. PILB HDTMA 0,1 % Al-Fe 1 mmole (1:1) and PILB HDTMA 0,1 % Fe 1 mmole have higher polymerization of O-Fe-O than PILB Al-Fe 1 mmole (1:1) and PILB Fe 1 mmole even though the difference is not significant.

The spectral region of 500 – 600 cm^{-1} show the presence of double ring structure which indicates there are pores in the pillared bentonite. Unfortunately, the pore structure of pillared bentonite does not differ significantly from it of fresh bentonite. The fact shows that pillaring process has not given pores with sufficient size.

Catalytic activity test

Phenol hydroxylation is oxidation of phenol by using H_2O_2. Molar ratio of phenol to H_2O_2 is 1 : 1. Reaction was conducted in batch mode in the presence of pillared bentonite as solid catalyst. The weight ratio of catalyst to phenol was 1:10, and concentration of phenol is 1 M. The reaction temperature was 70^oC, and reaction time was 4 hours. The observed variables were catalyst activity and selectivity. The catalyst activity was observed as phenol conversion, and the selectivity was observed as selectivity of wanted product (hydroquinone).

Table 2 Hydroxylation of phenol to hydroquinone and cathecol

Catalyst	Phenol Conversion (%)	Selectivity (%)		
		hydroquinone	cathecol	benzoquinone
Without catalyst	1.2	49.10	50.30	0.6
Fresh bentonite	4.4	47.00	52.40	0.6
PILB Fe 1 mmole	78.0	61.80	38.10	0.1
PILB Al-Fe 1 mmole (1:1)	72.7	59.77	40.20	0.03

PILB HDTMA 0,1% Fe 1 mmole	65.6	58.20	41.71	0.09
PILB HDTMA 0,1% Al-Fe 1 mmole (1:1)	76.7	63.37	36.60	0.03

Reaction condition: Catalyst/Phenol/H_2O_2 = 1/10/10
Percentage conversion and reaction selectivity were determined by HPLC analysis

In general, the presence of catalyst can increase reactant conversion and product selectivity. Table 2 shows phenol conversion and catalytic product selectivity (hydroquinone and cathecol) increase in the presence of catalyst. It is caused chemical adsorption in the catalyst pore surface will release energy so that it will decrease activation energy. Beside of the reason, Fe in the catalyst structure can oxidize phenol together with H_2O_2.

PILB Fe 1 mmole catalyst gives phenol conversion as high as 78% and the amount of Fe penetrates into bentonite is 4.8 mg/g solid. Whereas PILB HDTMA 0.1 % Fe 1 mmole catalyst reach phenol conversion 65.6 % and the amount of Fe introduces into solid is 5 mg/g solid. The amount of Fe which is introduced into PILB HDTMA 0.1 % Fe 1 mmole is slightly higher than that of PILB Fe 1 mmole catalyst but the phenol conversion of PILB HDTMA 0.1 % Fe 1 mmole is lower than that of PILB Fe 1 mmole. It is caused that phenol has been converted into catalytic product in the system with PILB HDTMA 0.1 % Fe 1 mmole. The selectivity of hydroquinone and cathecol of system which uses PILB HDTMA 0.1 % Fe 1 mmole in series are 58.2% and 41.7%, whereas those of PILB Fe 1mmole catalyst are 61.8% and 38.1%. This result describes that HDTMA molecule on PILB HDTMA 0.1 % Fe 1 mmole has not been very successfully disappeared during calcinations and oxidation process, since the selectivity of wanted product on PILB HDTMA 0.1 % Fe 1 mmole is lower than that of on PILB Fe 1mmole. This is supported by FTIR spectra which is the pore of PILB HDTMA 0.1 % Fe 1 mmole has not significantly created.

All modified bentonite catalyst will give better result (higher phenol conversion and CAT selectivity) compare to fresh bentonite. It shows that modification process (intercalation and pillarisation) give slightly effect to increase catalytic activity of fresh bentonite because of increasing bentonite pore size.

Based on this finding, it is proposed that Fe has participated in this reaction. HDTMA is expected to increase pore size and be able to support two bentonite layers before penetrating pillaring agent, but the experiment did not get optimal condition of material. It is proved by reaction products (HQ and CAT) which is produced by using catalyst with HDTMA is the same as that which is produced by using catalyst without HDTMA. It is

caused HDTMA can not be disappeared and give crowded pores in the bentonite structure. Because of that the reaction can not run effectively, because HDTMA has covered active sites of catalyst. This condition causes small amount of reactant can be contacted with active site of catalyst so that the reaction tends to follow non catalytic mechanism. In this study the presence of Al does not give significant increase in the activity of catalyst.

Conclusion

In this research, pilllarization process of bentonite using Fe has successfully given significant increase in the pore size of natural bentonite so that it increase the catalytic activity and product selectivity. The presence of Al and HDTMA in intercalation process does not give very significant effect to increase pore size and catalytic activity to the pillared-Fe bentonite.

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